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(54) Ultra low carbon boron steels (ULCB) for applications requiring extreme drawability and/or cold formability

(57) An ultra-low carbon boron steel comprises by weight per cent: not more than 0.01% C, not more than 0.01% Si, not more than 0.25% Mn, not more than 0.05% Al, approximately 0.0025% to 0.0035% N and between 0.0020% and 0.0050% B, the remainder being

iron and incidental elements and impurities, wherein the weight ratio of B:N is between about 0.68 and 0.90. The steel can be continuously cast and processed for applications requiring extreme drawability and cold formability.

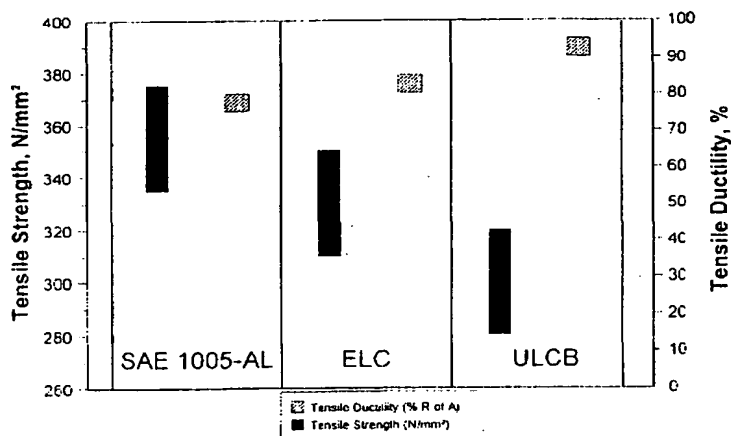


FIGURE 4

Description

[0001] The present invention relates to a continuously cast, boron treated ultra-low carbon steel (ULCB) for use in applications where:-

- (i) extreme drawability and / or
- (ii) cold formability is required.

[0002] More specifically, the invention relates to a steel having an ultra-low carbon content and a boron addition which has drawability and cold formability comparable to or better than that of conventional ingot cast rimming steels, other continuously cast rimming steel substitutes and aluminium treated low carbon cold heading steels. The present invention also relates to a process for producing such continuously cast boron treated ultra-low carbon steel as as-cast blooms, hot rolled billet, bar and rod.

[0003] There is a current trend within the steelmaking industry to move away from the traditional method of ingot casting and towards the newer, more efficient continuous casting method. Unfortunately, certain types of steel do not lend themselves to the continuous casting method and replacement steels have had to be developed. One of the steel types that is not suited to continuous casting, namely rimming steel, is utilised in the drawing of fine wires, e.g. for use in glass reinforcing mesh, and the drawing of larger wire diameters for subsequent use in cold heading operations to form components such as rivets. Rimming steels possess excellent drawability due to the presence of a virtually pure iron rim around the surface of the rod. This rim work hardens at a lower rate than the body of the steel during drawing and is very forgiving of any surface defects. The rim is developed by controlling the effervescence of CO gas during the solidification process. Unfortunately, the continuous casting process does not facilitate control of the gas evolution during solidification and a virtually pure iron rim cannot be formed by this method. Several rimming substitute steels have been developed for use in applications such as these, but as yet, none have possessed the drawability or cold formability of ingot cast rimming steels.

[0004] An objective of the present invention is to provide billet feedstock and a hot rolled steel bar or wire rod of a chemical composition giving lower tensile strength, higher ductility and a lower work hardening rate resulting in enhanced drawability and cold formability compared with the levels usually found in ingot cast rimming steels and other rimming steel substitutes. The resulting drawn wire products have a variety of applications. Large diameter drawn wires, for instance, can be cold headed to form rivets, whilst smaller drawn wires sizes (0.51, 0.66 and 0.71mm) find application in glass reinforcement mesh.

[0005] In accordance with the present invention there is provided a boron treated ultra-low carbon boron steel comprising by weight per cent: not more than 0.01 % C, not more than 0.01% Si, not more than 0.25% Mn, not more than 0.05% Al, approximately 0.0025% to 0.0035% N and between 0.0020% and 0.0050% B, the remainder being iron and incidental elements and impurities, wherein the weight ratio of B:N is between about 0.68 and 0.90.

[0006] Preferably the quantity of carbon is not more than about 0.007%.

[0007] Preferably the weight ratio of B:N is about 0.79. The free nitrogen available in the processed steel is preferably less than 0.001 % and preferably less than about 0.0007%.

[0008] In a second aspect, the invention is a steel billet, hot rolled bar or rod or cold drawn wire, the steel comprising by weight per cent: not more than 0.01 % C, not more than 0.01% Si, not more than 0.25% Mn, not more than 0.05% Al, approximately 0.0025% to 0.0035% N and between 0.0020% and 0.0050% B, the remainder being iron and incidental elements and impurities, wherein the weight ratio of B:N is between about 0.68 and 0.90.

[0009] In a third aspect, the invention is a method for manufacturing a rod or wire comprising the steps of;

continuously casting a steel having a composition by weight per cent of: not more than 0.01% C, not more than 0.01% Si, not more than 0.25% Mn, not more than 0.05% Al, approximately 0.0025% to 0.0035% N and between 0.0020% and 0.0050% B, the remainder being iron and incidental elements and impurities, wherein the weight ratio of B:N is between about 0.68 and 0.90;

producing the steel in the form of a billet suitable for further processing by hot rolling;

rolling the billet into a bar or rod at temperatures between 1100 and 830°C;

cooling at a rate sufficiently low to allow interstitial carbon to precipitate from solution;

drawing the rod to the desired wire diameter; and optionally

annealing the wire at a temperature suitable to develop the desired tensile strength and ductility in the wire product.

[0010] Ingot cast rimming steels have conventionally been used for extreme drawability applications. The inventors propose compositions of the present invention as continuously castable alternative steels for these purposes with comparable and in some cases superior properties to rimming ingot cast steels in these applications.

[0011] Figure 1 shows the work hardening curve for ULCB steel and ingot cast rimming steel (R06).

[0012] Figure 2 shows the ageing response of the ULCB and ingot cast rimming steel (R06) final wire.

[0013] Figure 3 shows the annealing response of the ULCB and ingot cast rimming steel (R06) final wire.

[0014] Figure 4 shows the tensile properties of 5.5mm ULCB, ELC (Corus™ grade) and SAE 1005-AL rimming substitute steel rod.

[0015] Steel materials according to the present invention may be used in the production of wires destined for use in two distinct and separate applications, namely:-

(i) applications requiring extreme drawability, e.g. production of fine wire feedstock (0.71-0.51mm diameter) for the manufacture of mesh for glass reinforcement mesh.

(ii) applications requiring a high degree of cold formability, e.g. production of larger diameter wire feedstock for the manufacture of rivets via a cold heading operation.

[0016] The requirements of the present invention will be fully described with reference to the individual applications, however, the examples do not restrict the present invention.

(i) ULCB Wire Rod for Extreme Drawability Applications

[0017] The following describes one suitable process route to obtain a wire for use in glass reinforcement made from the novel composition to which the present invention relates.

[0018] Steels of the previously described composition ranges are continuously cast into bloom and hot rolled to billet and then to 5.5 mm rod at temperatures between 1100 and 830°C using a continuous rod mill fitted with a Stelmor™ controlled cooling conveyor. The conveyor fan settings are kept relatively low so that the cooling rate on the conveyor is sufficiently slow to allow interstitial carbon to precipitate from solution, thus minimising any contribution to tensile strength in the end product.

[0019] The 5.5mm rod is descaled and drawn to 1.51mm using calcium soap then drawn to 0.51mm using sodium soap. The 0.51mm final wire may then be subsequently annealed at approximately 600-620°C to develop the required tensile strength and ductility in the wire end product.

[0020] The following gives the composition and mechanical properties of the rod and wire at the various stages of processing along with comparable data for an ingot cast rimming steel.

[0021] The product analyses of the rod and wire samples are shown in Table 1 as compared to an ingot cast rimming steel rod.

TABLE 1

Material	Composition (wt %)								
	C	Si	Mn	P	S	Al	B	O	N
ULCB Rod	0.006	<0.01	0.14	0.007	0.006	0.026	0.0023	0.0029	0.0033
Ingot Cast Rimming Steel Rod	0.021	<0.01	0.22	0.011	0.009	<0.005	<0.0005	0.0300	0.0017
Mo and Sn <0.005% and Cu <0.02%.									

Tensile Properties 5.5mm Rod

[0022] The tensile properties of the ULCB and ingot cast rimming steel rod samples are summarised in Table 2:-

TABLE 2

Sample	Average TS (N/mm ²)	Average R of A (%)
ULCB Rod	314	92
Ingot Cast Rimming Steel Rod	342	81

Microstructure

[0023] The microstructure of the ULCB rod consists almost entirely of ferrite grains (99.8 vol.%) with a very small amount of grain boundary/filamental carbide (0.2 vol.%).

The mean lineal intercept ferrite grain size are given in Table 3:-

TABLE 3

Sample	MLI Ferrite Grain Size	
	(mm ^{-1/2})	(μm)
ULCB Rod	6.1	27
Ingot Cast Rimming Steel Rod	8.1	15

Mechanical Properties of As-Drawn 1.51 mm wire

[0024] The mechanical properties of the as-drawn 1.51mm intermediate wire are given in Table 4. The 1.51mm intermediate wire was naturally aged at room temperature for up to 50 days. The change in tensile, torsion and reverse bend properties were followed throughout the ageing process. The changes in tensile properties are also given in Table 4 along with the changes in torsional and reverse bend properties.

TABLE 4

Sample		TS (N/mm ²)		R of A (%)		Bend Ductility (No. of Bends)		Torsional Ductility 100 d (Twists to Failure)	
		Ave	Range	Ave	Range	Ave	Range	Ave	Range
ULCB	As-Drawn	699	699	81	80-82	24	22-25	42	42
	Aged 1 day	686	680-691	76	76	24	23-25	42	42-43
	Aged 5 days	679	678-680	77	76-77	24	23-25	41	40-41
	Aged 11 days	716	707-724	77	77	24	23-25	42	42
	Aged 20 days	685	680-689	77	76-77	24	23-25	41	40-42
	Aged 50 days	701	688-714	77	76-78	25	24-26	41	41

[0025] A summary of all the observed properties is given below.

(a) Tensile Strength:-

The tensile strength of the 1.51 mm intermediate wire changes by no more than 37 N/mm² over the 50 day ageing period.

(b) Tensile Ductility:-

Following an initial drop, the tensile ductility (% R of A) of the 1.51 mm intermediate wire remains almost constant throughout the 50 day ageing period.

(c) Reverse Bend Ductility/Torsional Ductility:-

There was virtually no change in either reverse bend ductility or torsional ductility of the 1.51 mm intermediate wire throughout the 50 day ageing period.

Mechanical Properties of As-Drawn 0.51mm wire

[0026] The work hardening response of ULCB and ingot cast rimming steels during the drawing from 5.5mm rod to

0.51mm wire is represented graphically in Figure 1.

[0027] The mechanical properties of the as-drawn 0.51 mm ULCB final wire are given in Table 5 along with comparable data for as-drawn 0.51mm ingot cast rimming steel wire.

TABLE 5

Sample		TS (N/mm ²)		R of A (%)		Bend Ductility (No of Bends)		Torsional Ductility 200 d (Twists to Failure)	
		Ave	Range	Ave	Range	Ave	Range	Ave	Range
ULCB	As-Drawn	1070	1065-1075	77	75-78	14	14-15	64	58-72
	Aged 3 days	1037	1034-1039	74	72-75	13	12-14	63	63-64
	Aged 5 days	1039	1039	77	75-78	13	13-14	62	58-63
	Aged 12 days	1039	1034-1044	75	75	14	14	6	58-77
	Aged 20 days	1054	1054	74	72-75	13	13-14	68	64-70
	Aged 52 days	1049	1044-1054	78	78	14	13-15	71	65-78
Ingot Cast Rimming Steel	As-drawn	1273	1268-1278	59	59	9	9	57	54-63
	Aged 1 day	1278	1268-1288	59	59	10	9-11	45	41-51
	Aged 6 days	1322	1317-1327	59	59	11	11	64	58-64
	Aged 11 days	1287	1277-1297	59	59	10	9-11	47	39-54
	Aged 50 days	1251	1246-1256	61	59-63	10	9-12	50	48-55

[0028] The 0.51mm wire was naturally aged at room temperature for up to 50 days. The change in tensile, torsion and reverse bend properties were followed throughout the ageing process. The changes in tensile properties are given in Table 5 and presented graphically in Figure 2. The changes in torsional and reverse bend properties are also given in Table 5.

[0029] A summary of the observed properties is given below.

(a) Tensile Strength:-

The tensile strength of the ULCB 0.51mm final wire varies by no more than 31N/mm² over the 50 day ageing period, compared with a variation of 71N/mm² in the ingot cast rimming steel.

(b) Tensile Ductility:-

The tensile ductility of both the 0.51mm ULCB and ingot cast rimming steel final wire remains relatively unchanged during the 50 day ageing period. At ~76%, the level of tensile ductility in the ULCB steel is higher than the 59% found in the ingot cast rimming steel.

(c) Reverse Bend

There was virtually no change in the reverse bend ductility of either the ULCB or the ingot cast rimming steel wire throughout the 50 day ageing period.

(d) Torsional Ductility:-

The torsional ductility of the 0.51mm ULCB final wire showed a slight rise during the 50 day ageing period.

The torsional ductility of the 0.51mm ingot cast rimming steel final wire exhibited a large degree of scatter over the 50 day ageing period.

Mechanical Properties of Annealed 0.51mm wire

[0030] The tensile properties of laboratory annealed 0.51mm ULCB final wire are given in Table 6 along with comparable data for as-drawn 0.51mm ingot cast rimming steel wire and are presented graphically in Figure 3.

TABLE 6

Steel	Annealing Temperature (°C)	Tensile Strength (N/mm ²)		R of A (%)	
		Average	Range	Average	Range
ULCB	550	387	382-392	91	91
	575	392	392	90	89-90
	600	353	353	92	92
	625	314	312-315	93	92-93
	700	274	251-297	86	85-87
	800	245	243-248	85	82-87
Rimming Steel	550	319	317-320	85	83-86
	575	312	311-312	84	83-85
	600	292	291-293	88	87-88
	625	313	308-317	85	81-88
	700	260	256-264	80	78-82
	800	190	181-198	84	82-85

(ii) ULCB Wire Rod for Applications Requiring a High Degree of Cold Formability

[0031] The following describes one suitable process route to obtain a wire for use in applications requiring a high degree of cold formability (such as the production of rivets via a cold heading operation) made from the novel composition to which the present invention relates.

[0032] Steels of the previously described composition ranges are continuously cast into bloom and hot rolled to billet, rod and then to bar or rod at temperatures between 1100 and 830°C using a continuous rod mill fitted with a Stelmor™ controlled cooling conveyor. The conveyor fan settings are kept relatively low so that the cooling rate on the conveyor is sufficiently slow to allow interstitial carbon to precipitate from solution, thus minimising any contribution to tensile strength in the wire product.

[0033] The following gives the composition and mechanical properties of 5.5mm ULCB rod along with comparable data for other continuously cast cold heading grades.

[0034] Typical product analyses of ULCB, ELC (Corus grade) and SAE 1005-AL steels are shown in Table 7.

TABLE 7

Material		Composition (wt %)							
		C	Si	Mn	P	S	Al	N	B
ULCB	Typical	0.006	0.006	0.20	0.004	0.006	0.030	0.003	0.0035
	Min	-	-	0.15	-	-	0.020	-	0.0020
	Max	0.010	0.010	0.25	0.015	0.015	0.050	0.005	0.0050
ELC (Corus Grade)	Typical	0.010	0.010	0.20	0.007	0.010	0.030	0.003	-
	Min	-	-	0.15	-	-	0.020	-	-
	Max	0.030	0.020	0.25	0.025	0.025	0.050	0.007	-

TABLE 7 (continued)

Material		Composition (wt %)							
		C	Si	Mn	P	S	Al	N	B
SAE 1005-AL	Typical	0.040	0.010	0.25	0.015	0.018	0.035	0.004	-
	Min	-	-	0.20	-	-	0.020	-	-
	Max	0.060	0.050	0.40	0.035	0.035	0.050	0.007	-

[0035] Typical tensile properties of 5.5mm ULCB, ELC and SAE 1005-AL steel rod are summarised in Table 8 and represented graphically in Figure 4:-

TABLE 8

Steel	Typical Mechanical Properties	
	Tensile Strength (N/mm ²)	Tensile Reduction of Area (%)
ULCB	280-320	90-95
ELC	310-350	83-88
SAE 1005-AL	335-375	75-80

[0036] The true stress-strain relationship for low carbon steels can be represented by the following equation:-

$$\sigma = A \cdot \epsilon^n$$

[0037] The corresponding values for the ULCB and SAE 1005-AL steels are given in Table 9:-

TABLE 9

Steel Type	Values	
	A	n
ULCB	533.0	0.214
SAE 1005-AL	635.5	0.244

[0038] The additional drawability of ULCB enables increased reductions in diameter without the requirement of an intermediate annealing operation prior to the cold heading operation. For example, cold heading can be performed on direct drawn

[0039] ULCB as compared with inter-annealed SAE 1005-AL. In addition, ULCB may also enable the production of more complex components without the risk of cracking.

[0040] The foregoing describes examples of a suitable manufacturing process and properties of just some compositions according to the present invention and is not intended to be limiting of the true scope of the invention as claimed in the appended claims.

Claims

1. An ultra-low carbon boron steel comprising by weigh per cent:
not more than 0.01% C, not more than 0.01% Si, not more than 0.25% Mn, not more than 0.05% Al, approximately 0.0025% to 0.0035% N and between 0.0020% and 0.0050% B, the remainder being iron and incidental elements and impurities, wherein the weight ratio of B:N is between about 0.68 and 0.90.
2. An ultra-low carbon boron steel as, claimed in claim 1 wherein the quantity of carbon is not more than about 0.007%.
3. An ultra-low carbon boron steel as claimed in claim 2 wherein the C content is between about 0.004% and 0.005%.

4. An ultra-low carbon boron steel as claimed in any preceding claim wherein the weight ratio of B:N is between 0.68 and 0.90.
5. An ultra low carbon boron steel as claimed in claim 4 wherein the B:N ratio is about 0.79.
6. An ultra-low carbon boron steel as claimed in any preceding claim wherein the free nitrogen available in the processed steel is less than 0.001%.
7. An ultra low carbon boron steel as claimed in claim 8 wherein the free nitrogen available in the processed steel is less than 0.0007%.
8. A billet, bar, rod or wire comprising an ultra low carbon boron steel as claimed in any preceding claim.
9. A method for manufacturing a wire comprising the steps of;
- continuously casting an ultra low carbon steel of the composition as claimed in any one of claims 1 to 7;
rolling the cast steel into a billet then to rod at a temperature of between about 1100 and 830°C;
cooling at a rate sufficiently low to allow interstitial carbon to precipitate from solution;
drawing the cooled rod to the desired wire diameter; and optionally
annealing the wire at a temperature suitable to develop the desired tensile strength and ductility in the wire product.
10. A method for providing a cold-headed metal article comprising the steps of:
- continuously casting an ultra-low carbon steel of the compositions as claimed in any one of claims 1 to 7;
rolling the cast steel into a billet then to bar or rod at a temperature of between about 1100 and 830°C;
cooling at a rate sufficiently low to allow interstitial carbon to precipitate from solution;
drawing the cooled bar/rod to a desired wire diameter;
selecting a portion of the wire for the cold-headed product; and
cold heading the selected portion to form the product.
11. An ultra low carbon boron steel substantially as described herein.
12. A wire comprising ultra low carbon boron steel substantially as described herein.
13. A cold headed metal article comprising an ultra-low carbon boron steel substantially as described herein.
14. A method for manufacturing a wire substantially as described herein.
15. A method for manufacturing a cold-headed metal article substantially as described herein.

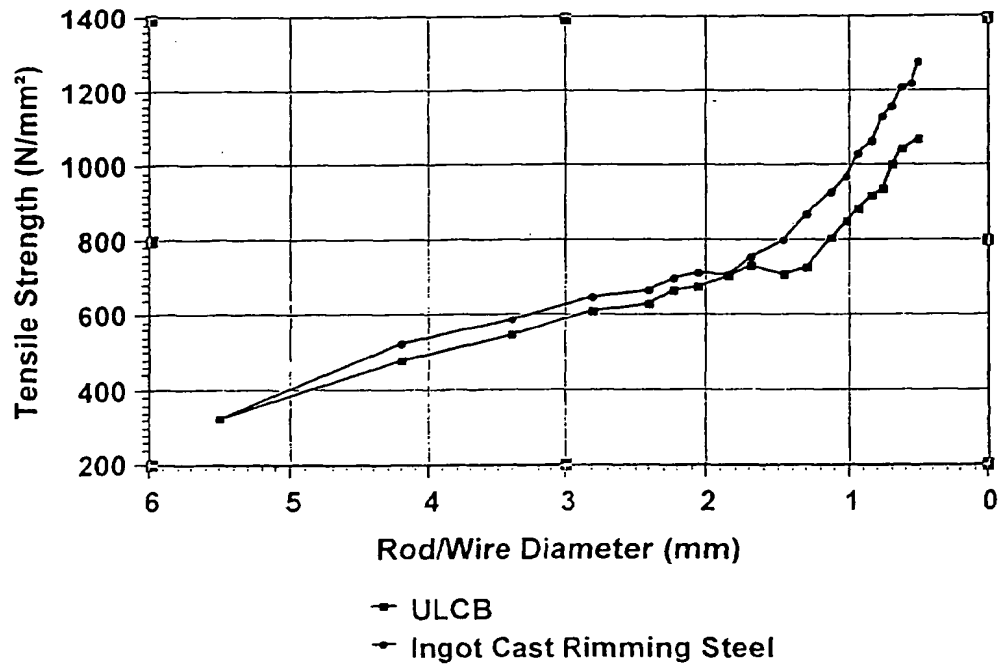


FIGURE 1

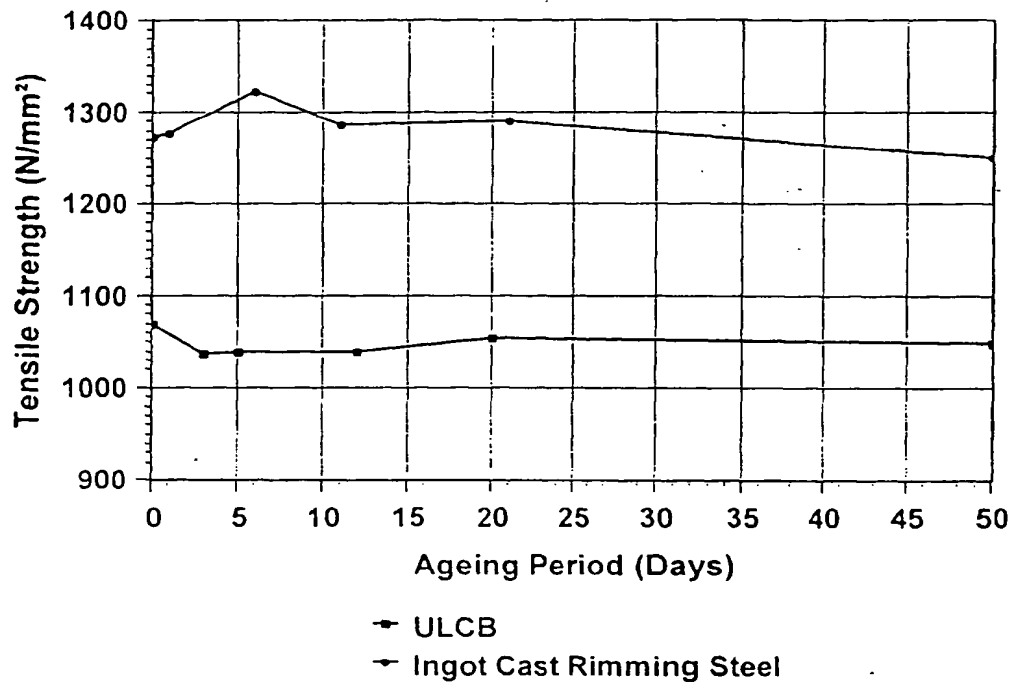


FIGURE 2

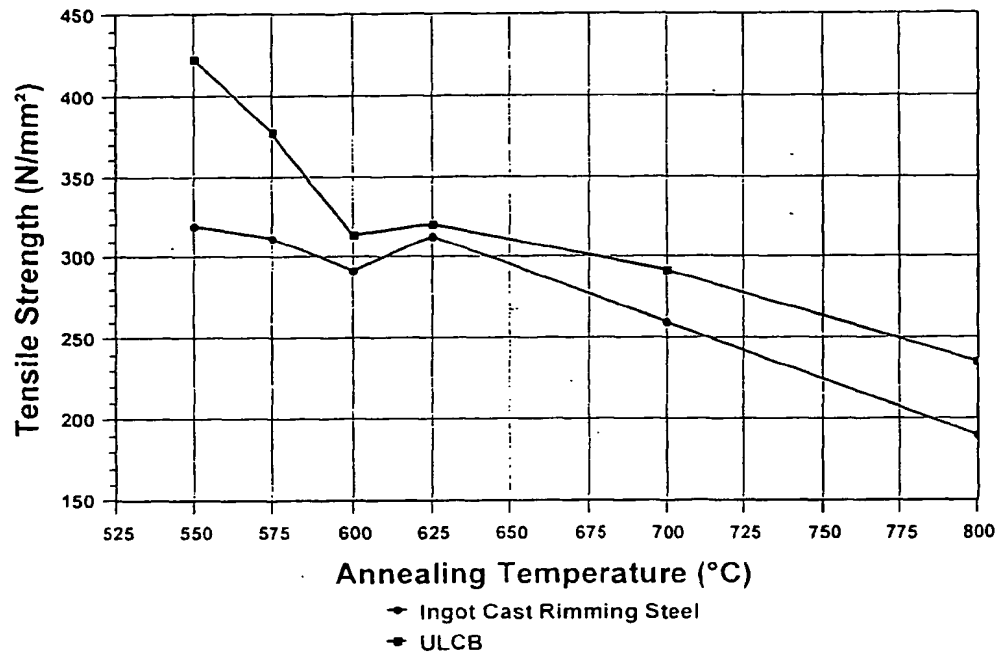


FIGURE 3

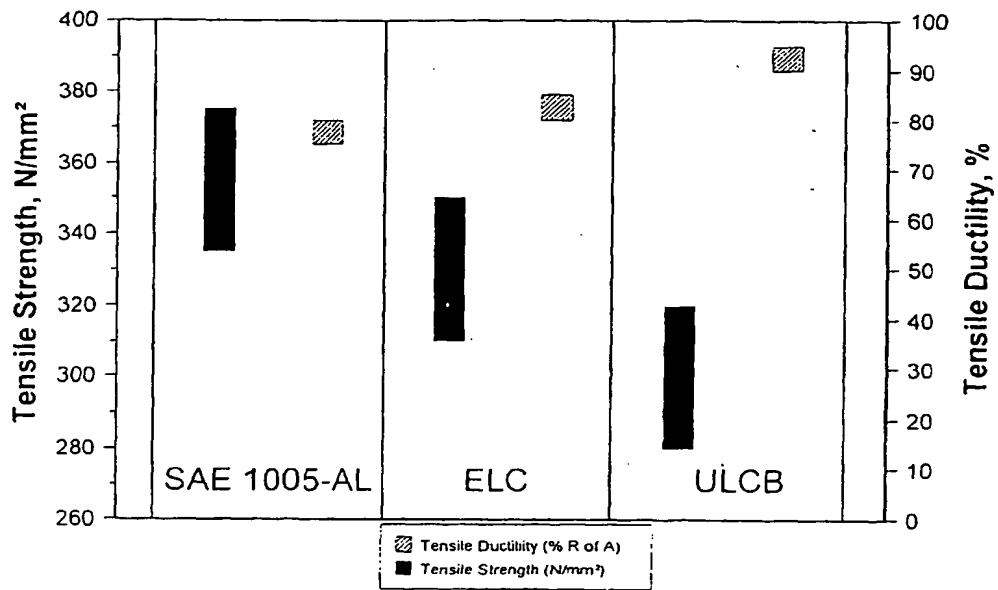


FIGURE 4



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EUROPEAN SEARCH REPORT

Application Number
EP 01 30 2434

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) -& JP 11 100637 A (NIPPON STEEL CORP), 13 April 1999 (1999-04-13) * abstract; example D *	1-15	C22C38/00
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 05, 31 May 1999 (1999-05-31) -& JP 11 050195 A (NIPPON STEEL CORP), 23 February 1999 (1999-02-23) * abstract; example B *	1-15	
X	LU 86 384 A (CENTRE RECH METALLURGIQUE) 7 December 1987 (1987-12-07) * page 1, paragraph FIRST * * page 2, paragraph SECOND *	1-15	
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 088 (C-276), 17 April 1985 (1985-04-17) -& JP 59 219411 A (SHIN NIPPON SEITETSU KK), 10 December 1984 (1984-12-10) * abstract; example D *	1-15	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 007, no. 232 (C-190), 14 October 1983 (1983-10-14) -& JP 58 123855 A (KAWASAKI SEITETSU KK), 23 July 1983 (1983-07-23) * abstract *		C22C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 18 July 2001	Examiner Ashley, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 082 (C-275); 11 April 1985 (1985-04-11) - & JP 59 215463 A (AZUMA SEIKOSHO:KK;OTHERS: 01), 5 December 1984 (1984-12-05) * abstract *		
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 18 July 2001	Examiner Ashley, G
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 01 30 2434

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18-07-2001

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 11100637	A	13-04-1999	NONE	
JP 11050195	A	23-02-1999	NONE	
LU 86384	A	07-12-1987	BE 905964 A	17-06-1987
JP 59219411	A	10-12-1984	JP 61058527 B	12-12-1986
JP 58123855	A	23-07-1983	NONE	
JP 59215463	A	05-12-1984	NONE	

EPO FORM P0139

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82